



Dimethyl carbonate via transesterification of propylene carbonate with methanol over ion exchange resins

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ABSTRACT

The transesterification of propylene carbonate with methanol to form dimethyl carbonate has been carried out in the presence of strong basic ion exchange resins as heterogeneous catalysts at low temperatures. Experiments have been carried out in a 75 mL autoclave as well as in a continuous flow fixed bed reactor. Temperatures were varied between -20 and 40°C without any additional pressure. The molar ratio of methanol and propylene carbonate was adjusted between 8:1 and 4:1. The ion exchange resins showed a high activity even below 0°C when OH^- is used as counter ion. Leaching tests resulted in a complete hold of the conversion after removing the catalyst. In the continuous reactor the catalysts suffered from a rather fast deactivation within one week due to the transformation of the counter ion hydroxide to carbonate. However, a regeneration of the catalyst using different basic liquids was possible resulting in a complete recovery of its catalytic activity.

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1. Introduction

Dimethyl carbonate (DMC) is a promising chemical for a broad variety of applications. It can be used as solvent for the production of electrolytes for lithium-ion-batteries [1], as a non-toxic polar solvent, or as a methylating agent, e.g. to produce urethanes or carbamates [2]. Thereby, DMC could replace toxic chemicals such as dimethylsulfate, methyl iodide, or phosgene which is used, e.g. for the production of diisocyanates needed for polyurethanes [3,4]. In addition, its utilization as a non-toxic octane booster in fuels replacing MTBE has been discussed [5]. There are many different ways to synthesize DMC such as carbonylation of methanol with carbon monoxide and oxygen [4,6,7] or the reaction of urea with methanol [8–10]. The reaction we were focusing on is the transesterification of propylene carbonate (PC) with methanol. Knifton and Duranleau reported on several different catalysts, both heterogeneous and homogeneous, which are active for this reaction [11]. Thereby, propylene glycol is obtained as an inevitable by-product, which could be recycled to produce PC on the one hand. On the other hand, this valuable chemical could be sold as a frost protecting agent or as an ingredient of cosmetics [12]. Knifton et al. stated that basic

ion exchange resins can be active catalysts for the transesterification of a cyclic carbonate with methanol at temperatures of around 100 – 120°C . Thereby, most of the catalysts contained chloride as counter ion.

In our work, we focused on strongly basic quaternary ammonium ion exchange resins with hydroxide counter ions, which should be more active than the weaker basic chloride counter ions. Because the hydroxide form of such strongly basic ion exchange resins is not as stable as its chloride form, the applicable temperature was limited to 40 – 60°C or even lower temperatures. Above 60°C decomposition proceeds by Hofmann elimination to produce an alcohol and a tertiary amine [13].

2. Experimental

2.1. Materials and analytics

Methanol and propylene carbonate were used as purchased (reagent grade, >99%, Aldrich). The basic catalysts were obtained from Rohm&Haas (Amb. 26OH, Amb. 70, Amb. DT, Amb. 39 wet), the Mitsubishi Chemical Corporation (PA312L/OH), and the DOW Chemical Company (MAR-MSA, MS-MP725A). For GC analysis, DMC (reagent grade >99%, Merck), propylene glycol (p.a. grade, >99.5%, Fluka), and 1,4-dioxane (HPLC grade, VWR) were used as purchased.

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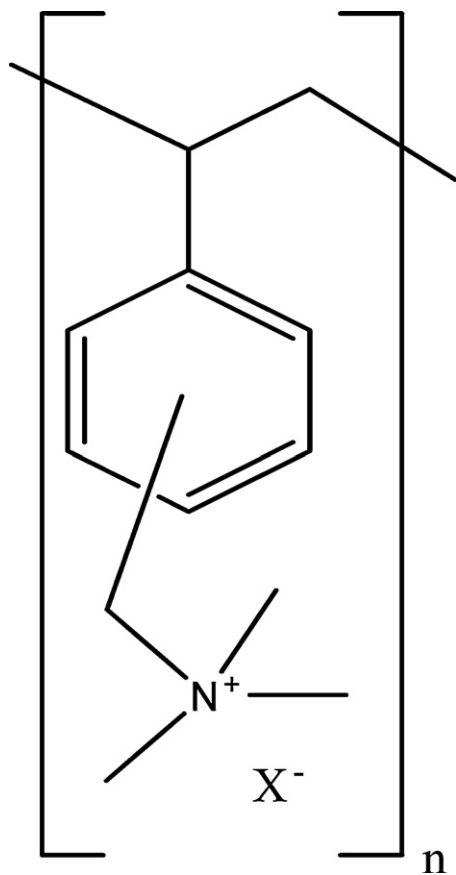


Fig. 1. Strong basic type 1 anionic ion exchange resin.

All conversions and selectivities were calculated based on GC analysis. The measurements were carried out using a HP 6890 Plus chromatograph with a DB 23 (60 m J&W US 1308015H) column and a FID detector. The internal standard for calculating correction factors was 1,4-dioxane.

2.2. Basic ion exchange resins

The tested basic ion exchange resins consisted of a polystyrene backbone with different amounts of divinylbenzene as crosslinker. All four ion exchange resins used were from macroporous type to ensure the limitation of diffusion problems. The active groups were strong basic, type 1 quaternary ammonium groups with hydroxyl or chloride counter ions (see Fig. 1). These catalysts differed slightly in their amount of exchange capacity. Further investigations for characterization of these commercial available catalysts have not been carried out due to the fact that such information are disclosed by the companies in their data sheets.

2.3. Calculation of the thermodynamic equilibrium

The reaction of PC and methanol yielding DMC is limited by the thermodynamic equilibrium. A huge quantity of substance data for PC is given in the literature, exhibiting a large scatter. Since no reliable experimental data were available and Benson's group increment method lacks essential parameters, DFT calculations were applied to obtain the Gibbs energy of the reaction. These calculations were performed using TURBOMOLE (Version 6.2, 2010, a development of the University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007; available from <http://www.turbomole.com>) with B3-LYP functional and def2-TZVPP basis set.

The activity coefficients needed for the calculation of the equilibrium conversion were calculated using the models COSMO-RS [14] and UNIFAC, both giving similar results. The fugacity coefficients were calculated using the Redlich–Kwong equation of state.

2.4. Set-up for the batch experiments

A batch-wise procedure was applied in order to determine the reaction rate at low temperatures of about 40 °C. As can be seen in a previous work [11], at temperatures of about 100 °C the transesterification of ethylene carbonate with an excess of methanol (1:4) resulted in a conversion of around 60% within 30–60 min. The conversion of the bulkier PC should be slower. Considering the thermodynamic calculations (Section 2.2) a molar ratio of 8:1 of methanol and PC is used at the beginning. 35 g of this mixture in a round bottom flask containing a magnetic stirring bar was heated to the desired temperature. Once this temperature was reached, 1.0 g of the respective catalyst was added and the flask was sealed. Different samples of the liquid phase were taken by means of a syringe equipped with a syringe filter (0.45 µm pore diameter) to avoid catalyst contaminating the sample.

2.5. Set-up for the continuous flow experiments

To examine the lifetime of the basic catalysts, a continuous flow set-up has been installed. The starting materials were mixed previously and stored at room temperature. Blank-tests showed, that no reaction takes place without a catalyst at temperatures up to about 100–120 °C. Therefore the mixed starting materials will not react until they reach the catalyst bed. The molar ratio of methanol to PC varied between 8:1 and 4:1. The catalyst was filled into the reactor and covered with methanol. Due to the results of the batch experiments, the weight hourly space velocity (WHSV) of PC was adjusted to values between 0.8 and 1.7 h⁻¹. After an induction period of around 2 h, liquid samples were taken from the reactor outlet. The mass balance was calculated several times and reached an average value of 98.8%. Therefore the formation of gaseous products is negligible and therefore taking gas samples were not necessary

3. Results and discussion

3.1. Results of the DFT calculations

At low pressures the system is partly vaporized. In this case mainly methanol, as the component with the lowest boiling point, is removed from the liquid phase. Hence the methanol concentration in the liquid phase is decreasing and the equilibrium is shifted toward the reactants. Therefore, it is desired to avoid vaporization by applying sufficient pressure. For the reaction temperatures used in this work, the pressure, that is needed to avoid vaporization is below atmospheric pressure, e.g. 0.3 bar at 40 °C. At this temperature and atmospheric pressure, the position of the thermodynamic equilibrium for a molar ratio of methanol to PC of 8:1 allows a PC conversion of 64%. For reaction temperatures higher than 65 °C, measures have to be taken to keep the system in the liquid phase.

The intermediate products, 2-hydroxypropyl methyl carbonate and 1-hydroxypropan-2-yl methyl carbonate, are both unstable in terms of thermodynamics. Therefore, their amount in the equilibrium mixture is very low. Nevertheless, the reaction mixture may contain significant amounts of the intermediates if the second reaction step is significantly slower than the first step. The decomposition of PC to propylene oxide and carbon dioxide is not favored thermodynamically at low temperatures. However, if the reaction temperature exceeds 100 °C at atmospheric pressure, the decomposition is favored thermodynamically.

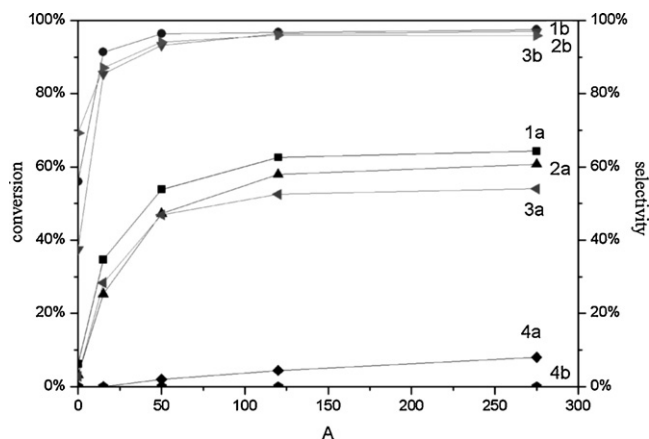


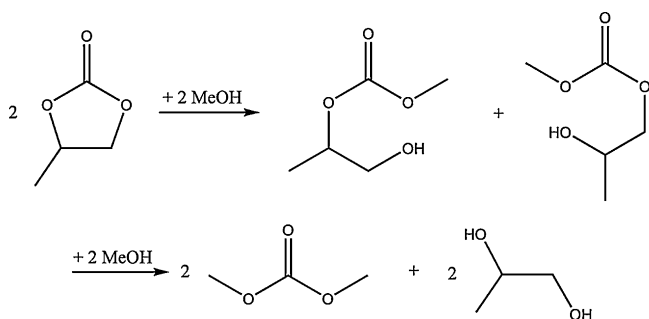
Fig. 2. Conversion and selectivity for DMC over reaction time. Temperature 40 °C, 1 g catalyst, MeOH:PC 8:1, 10.5 g PC. (a) Conversion, (b) selectivity, (1) Amberlyst 26 OH (2) PA312L/OH (3) MS-MP725A/OH (4) MAR-MSA/Cl.

3.2. Batch experiments

The conversion of PC and the selectivity for DMC over reaction time in the experiments carried out at 40 °C are shown in Fig. 2.

The three ion exchange resins having hydroxide counter ions exhibit comparable activity and convert about 55–65% of the PC within 2–5 h. The highest reaction rates were realized in the first hour with 80–90% of the reaction taking place. The selectivities to form DMC were very similar to each other for these ion exchange resins. Starting from low level at the beginning of the reaction, they rose to 90% after 15 min and reached around 97% after a reaction time of 1 h. The by-products which were detected throughout the experiments were the two intermediate products which are obtained by one transesterification with methanol (see Scheme 1) but no other side-products could be detected.

The catalytic performance of the ion exchange resin in its chloride form (no. 4) differed strongly from the other catalysts. It exhibited significantly lower activity and converted only around 10% of the PC. The reaction rate was much lower and the second transesterification seems to be the rate determining step. No DMC could be detected in the product mixture resulting in a selectivity of 0%. These experiments clearly indicated the superior catalytic activity of hydroxide form ion exchange resins in the transesterification of PC with methanol compared with ion exchange resins having chloride counter ions. The experimental results which were obtained with the hydroxide containing ion exchange resins were very similar to the calculated expected thermodynamic equilibrium. This is a very interesting result, because of the large scatter of thermodynamic data regarding PC and shows, that DFT calculations are a suitable instrument for predicting the thermodynamic data of this carbonate.



Scheme 1. Transesterification of PC with methanol including the two intermediate products.

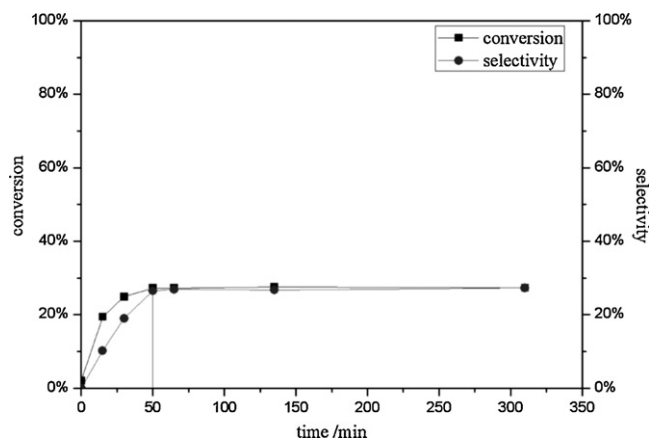


Fig. 3. Conversion of PC and selectivity to DMC in the leaching experiment. The vertical line indicates the time of catalyst removal. Temperature –5 °C, 1.5 g catalyst, MeOH:PC 4:1, 21 g PC.

It was necessary to ensure, that the catalyst does not decompose and leach, thereby acting as a homogeneous base. Therefore, a hot filtration test with 1.5 g of Amberlyst 26 OH has been performed and conversions as well as selectivities were monitored. The result of the experiment is shown in Fig. 3.

The reaction rate was lower than at 40 °C (see Fig. 2), but like in the previous experiments the conversion and the selectivity were rising until filtration of the catalyst. Afterwards the reaction came to a complete stop, without even converting the quite unstable intermediates to either the product or back to the starting material. This was a strong indication for an entirely heterogeneously catalyzed reaction.

3.3. Results of the continuous flow experiments

As the batch experiments showed a remarkably high activity even below room temperature, the reaction was carried out in a continuous fixed bed reactor. The results of the experiment are illustrated in Fig. 4.

Fig. 4 illustrates very clearly that the activity of the catalyst dropped to half of its initial activity within one day. Even due to the significant decrease of the catalyst activity no side reactions are observed. The loss of the DMC selectivity was due to the increased formation of the two intermediates which reached significant selectivities over time on stream (TOS). Despite the low temperature of –10 °C the conversion and selectivity, at the

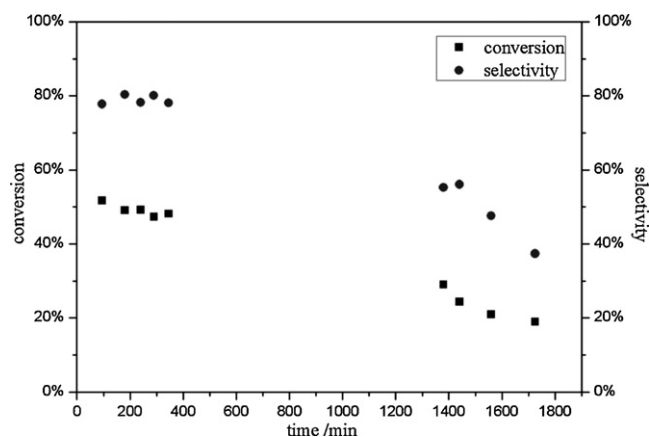


Fig. 4. Conversion of PC and selectivity to DMC in a continuous fixed bed reactor. Temperature –10 °C, 10 g Amberlyst 26 OH, MeOH:PC 8:1, volume flow rate 60 mL/h, WHSV = 1.7 h^{–1}.

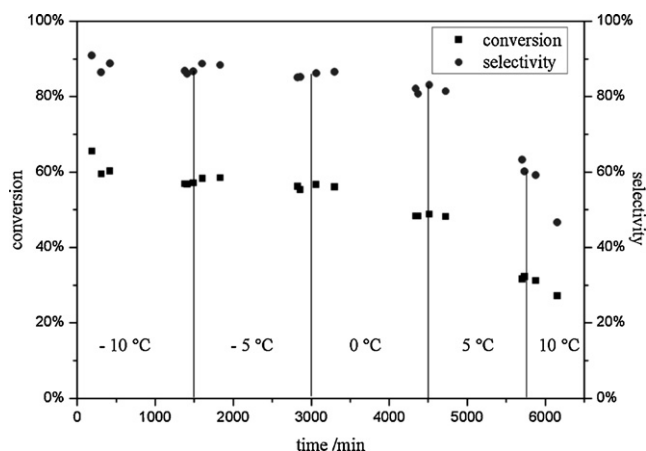


Fig. 5. Conversion of PC and selectivity to DMC in a continuous flow fixed bed reactor. Temperature -10 to $+10$ °C, 15 g Amberlyst 26 OH, MeOH:PC 4:1, volume flow rate 30 mL/h, WHSV = 0.9 h^{-1} .

beginning of the reaction, were almost the same as in the batch experiments (compare with Fig. 2). This demonstrated that with hydroxide as counter ion the starting activity of the catalyst was very high even at low temperatures and that the reachable conversions are very close to the expected values calculated by means of the DFT measurements.

The decreasing activity of the catalyst may have several reasons. On one hand it is possible that even though the temperature was very low, functional groups may have been split off the polymer backbone and have been washed out. On the other hand polymerization of propylene glycol (PG) may have occurred. Thus, the surface of the catalyst would be covered with polyether and the active sites would not be accessible after a few hours. The reaction of the hydroxide counter ions with the reaction mixture could be another reason for the decreasing activity. Thereby the hydroxide ions might react with one of the carbonates to form carbonate counter ions for the ammonium groups of the ion exchange resins. Carbonate ions are less basic than hydroxide ions and therefore the activity could decrease significantly.

To enhance the catalyst service time, the volume flow was reduced and the temperature was increased every 24 h. The results are depicted in Fig. 5.

The increase of the PC concentration in the reacting mixture in combination with the reduction of the volume flow resulted in almost the same yield of DMC based on PC as in the last experiment. At the same time, the excess of methanol could be reduced. After every 24 h the temperature was increased by 5 °C to counter the decrease of the catalyst activity. The catalyst activity improved slightly after increasing temperature (around 2% conversion per 5 °C). However, the catalyst deactivation also increased with the temperature. At 0 °C the catalyst deactivation was almost twice as fast and at +5 °C it was four times faster. Therefore, running the reaction with a temperature ramp was not a suitable method to increase the service time of the Amberlyst 26 OH between -10 and $+10$ °C.

The same experiments were carried out over Residion PA312L/OH ion exchange resin. This catalyst behaved very similar as Amberlyst 26 OH. Both catalysts have the same functional groups and the same backbone polymer but a somewhat different amount of crosslinkers. Therefore, in accordance with the experiments using the Amberlyst 26 OH (see Fig. 4), the volume flow was set to a lower level. This should result in a service time of more than four days in case of the Amberlyst demonstrated in Fig. 6.

As the volume flow was lower and therefore the effective service time was increased in comparison with the experiment using

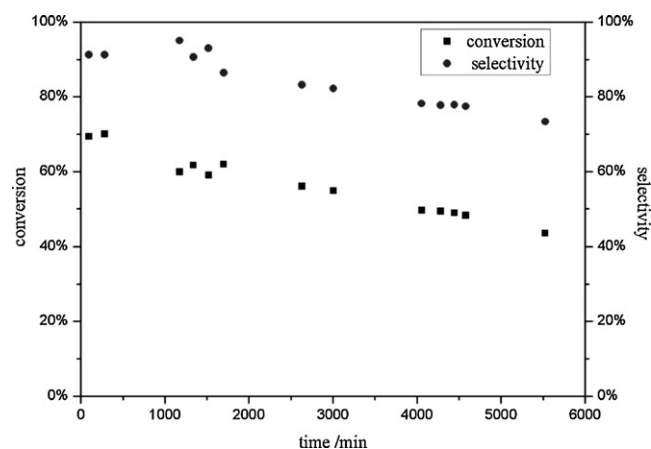


Fig. 6. Conversion of PC and selectivity to DMC in a continuous flow fixed bed reactor. Temperature -10 °C, 15 g PA312L/OH, MeOH:PC 8:1, volume flow rate 30 mL/h, WHSV = 0.9 h^{-1} .

the Amberlyst 26 OH, the conversion and selectivities as indicated in Fig. 6 were higher than the ones depicted in Figs. 4 and 5. The higher initial conversion of 70% was expected for the same reasons. The deactivation rate of the catalyst was around 5–7% per day and was comparable to the deactivation rate of the Amberlyst 26 OH (compared with Fig. 5). Because of the constant temperature there was no acceleration of the deactivation after three to four days. Due to the similarities of the two catalysts PA312L/OH and Amberlyst 26 OH, it could be assumed, that the mechanisms for the deactivation are identical.

For the investigation of the temperature dependence of PA312L/OH, the same reaction conditions were chosen as for the Amberlyst 26 OH (see Fig. 5). Therefore the comparison of the two experiments was possible. The results depicted in Fig. 7 indicated a high similarity to the Amberlyst 26 OH.

As in previous experiments, the temperature was increased by 5 °C after every 24 h, indicated by the vertical lines in the diagram. The conversion and the selectivity at low temperatures were almost identical for both catalysts. However, the initial activity of the Amberlyst 26 OH was slightly higher. Therefore, the PC conversion was around 10% higher for the first two days of this experimental set. When the temperature was increased to 0 °C and above, the performance of the two catalysts became different. The deactivation rate for the PA312L/OH was significantly faster and reached a loss of around 20% of the conversion in 24 h. Upon increase of the

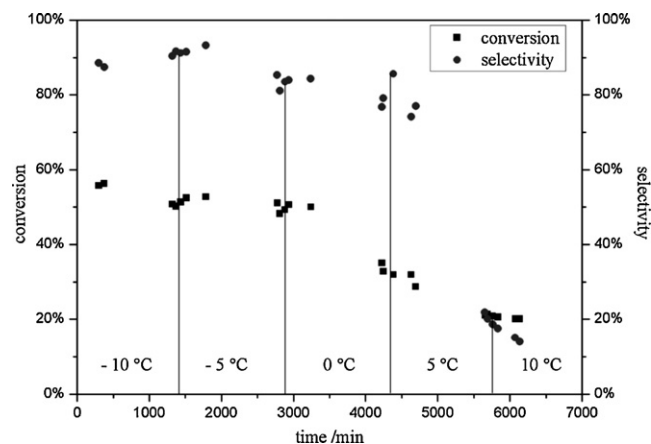


Fig. 7. Conversion of PC and selectivity to DMC in a continuous flow fixed bed reactor. Temperature -10 to $+10$ °C, 15 g PA312L/OH, MeOH:PC 4:1, volume flow rate 30 mL/h, WHSV = 0.9 h^{-1} .

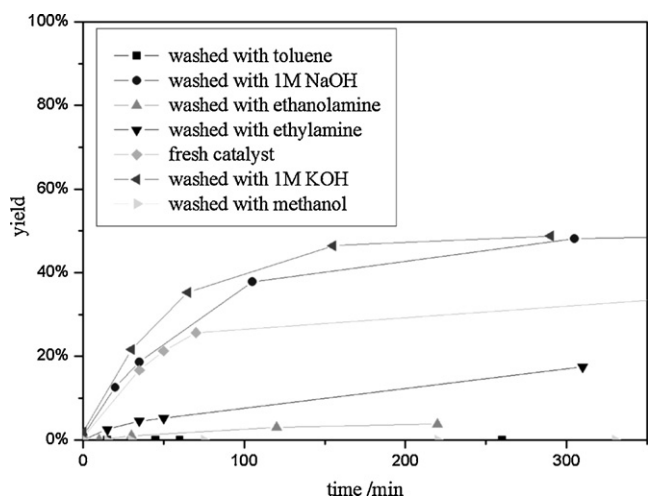


Fig. 8. Yield of DMC in a batch reaction after catalyst regeneration. Temperature +20 °C, 1.5 g PA312L/OH, MeOH:PC 4:1, 21 g PC.

temperature to +10 °C, the drop in conversion declined and reached a minimum at around 20% conversion. Meanwhile, the selectivity decreased rapidly, too. Again, side reactions were not the reason for this decline in selectivity, as no side products were observed in the product mixture. In contrary, the amounts of the two intermediate products were increasing reaching almost 90% selectivity at the end of the fourth day. Therefore, it could be concluded, that PA312L/OH is significantly more temperature sensitive than the Amberlyst 26 OH, even though both catalysts exhibited the same trends for conversion and selectivity.

3.4. Recycling of the catalyst

As both continuously tested catalysts were almost totally deactivated after one week, a regeneration of the catalyst was mandatory for recycling the catalyst. The method of choice depended on the deactivation pathway taking place (see Section 3.1). If an oligo- or polymerization of the starting material or the product have occurred, it may be possible to wash off the blocking organic materials using suitable solvents. Once the active sites are accessible for the starting material again, the activity should be restored. If on the other hand the hydroxide ions were forming carbonates or other less basic counter ions for the ammonium groups of the ion exchange resin, the activity could be restored by exchanging the formed ions with fresh hydroxide ions. In this case, washing with diluted alkaline bases should regenerate the catalytic activity. It was also possible that, despite the low temperatures, a decomposition of the functional groups occurred. In this case, none of the previously mentioned regeneration methods should lead to an increase in catalytic activity. However, the elimination of the functional groups could be reversible. Then washing with amines should lead at least to a partially regenerated catalytic activity.

Samples (1.5 g each) of the used and deactivated catalyst PA312L/OH from the previous experiment (see Fig. 7) were treated with different solvents and solutions like toluene, KOH or ethanolamine as shown in Fig. 8. Subsequently, all catalysts were efficiently washed with methanol until the eluate was free of used solvent or solution. Afterwards the treated catalysts were used in a batch experiment as described in Section 2.3. These experiments proved that a regeneration of the catalyst by washing with toluene or methanol was not possible. In these cases no DMC is obtained. The deactivated catalyst only forms the two intermediate products, but does not have enough activity for the second transesterification.

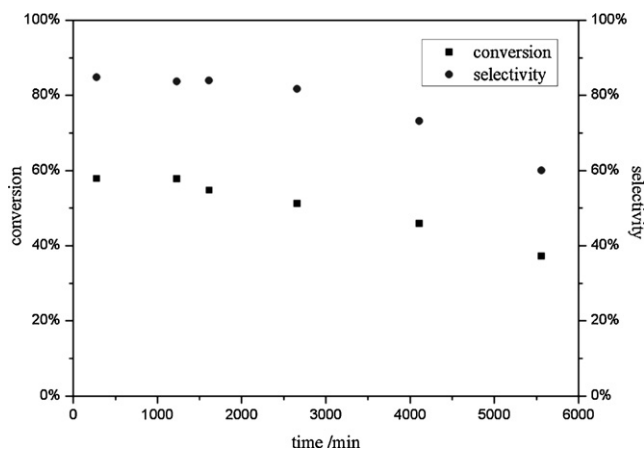


Fig. 9. Conversion of PC and selectivity to DMC using the regenerated catalyst in a continuous flow fixed bed reactor. Temperature –10 °C, 15 g PA312L/OH (regenerated), MeOH:PC 4:1, volume flow rate 30 mL/h, WHSV = 0.9 h⁻¹.

Washing with aqueous solutions of ethanolamine or ethylamine resulted in a partial regeneration of the catalyst, but the regained activity is significantly lower than the initial activity of the fresh catalyst.

However, washing the used catalyst with aqueous solutions of alkali hydroxides led to a full regeneration of the catalyst. Even after intensive washing with methanol until the alkali metal hydroxide solution has been completely washed out of the ion exchange resin, the gained activity was in fact somewhat higher than the initial activity of the catalyst. This clearly demonstrated that the main reason for the deactivation of the catalyst under the chosen reaction conditions was the transformation of the hydroxide counter ions to less basic anions. Furthermore, these results indicated, that the unused catalyst was already partially deactivated, probably due to adsorption of gaseous carbon dioxide while kept in storage. The easy ion exchange back to the fully regenerated OH⁻ form of the ion exchange resins using 1 M solutions of alkali hydroxide demonstrated that thermal decomposition and blocking of the active sites due to polymerization were negligible. The partial recovery of the catalytic activity when washed with aqueous solutions of ethanolamine or ethylamine could be explained with the basicity of the dissolved amines due to the fact that hydroxide ions can replace to some extent the less basic anions in the ion exchange resin.

In order to verify, that the less basic counter ions on the resin formed during the reaction were carbonates, a simple test with a barium hydroxide solution has been carried out. The used PA312L/OH catalyst was washed with methanol until the eluate was free of PC and DMC. Afterwards the resin was treated with diluted hydrochloric acid resulting in the formation of gaseous products. The emerged gas was bubbled through an aqueous solution of barium hydroxide, followed by a precipitation of barium carbonate. This result proved, that the deactivation of the used ion exchange resins is caused by a reaction of the hydroxide counter ions to form carbonate ions.

Concerning these results, the used PA312L/OH was regenerated using a 1 M aqueous solution of potassium hydroxide and washed with methanol afterwards. This fully regenerated catalyst was recycled.

The reaction conditions were the same as in the previous experiment (see Fig. 7) with the exception of a constant temperature rather than a rising temperature program. The initial values for the conversion and selectivity of the regenerated catalyst (see Fig. 9) were the same as in the previous experiment. Due to the constant low temperature, the decrease in catalytic activity was almost

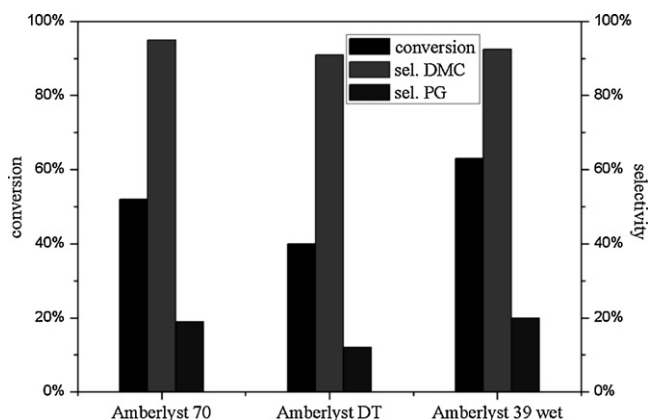


Fig. 10. PC conversion and selectivity to DMC and propylene glycol (PG) in an auto-clave reaction. Temperature 130 °C, autogeneous pressure, 1 g catalyst, MeOH:PC 8:1, 5.5 g PC, 120 min.

linear. However, it was slower than in the previous experiments. According to these results, the regeneration of the catalyst was successful. If the regained activity had been caused by remaining potassium hydroxide, the activity would have dropped very fast when washing out the homogenous base.

3.5. The comparison with acidic catalysts

The strong basic ion exchange resins showed a very high activity. When comparing these results with the results obtained with strong acidic ion exchange resins, several differences became apparent. The most obvious difference was the lower activity of the acidic catalysts. At temperatures of -10 to 40 °C almost no catalytic effect was observed and no DMC was produced. Therefore, higher temperatures of around 110 – 130 °C had to be used for the acidic catalysts. Fig. 10 depicts the results for the three used acidic ion exchange resins.

The conversion after 2 h reaction time differed between 40 and 65%. The comparison with the results of the basic ion exchange resins at 40 °C showed that the reaction rates were almost the same, but the selectivities to form PG have been different. While the selectivity for DMC and PG were almost the same in each experiment carried out over the basic ion exchange resins (and is therefore not mentioned in the diagrams), the selectivity to PG was very low when using acidic ion exchange resins probably due to oligomerization and polymerization reactions. It is likely, that those oligomers and polymers deposited on the catalyst. The catalyst showed a high weight gain and after a 48 h Soxhlet extraction with *n*-heptane the eluate contained many fragments of high molar mass as proved by GC–MS measurements. Therefore, it could be concluded, that basic ion exchange resins are not only far more active than their acidic counterparts, but revealed a much higher selectivity for the by-product PG. Despite this, a polymerization of PG is not necessarily a disadvantage. The production of the polyether is removing PG from the product mixture, therefore the accessible conversions are not

limited by the calculated thermodynamic equilibrium. At higher temperatures and longer reaction times an almost full conversion of PC could be achieved. However, as PG is a valuable by-product, it is not economic to produce oligomers which need to be extracted from the catalyst.

4. Conclusion

The experiments carried out during this research clearly demonstrated, that strong basic ion exchange resins are capable of catalyzing the transesterification of propylene carbonate with methanol to form DMC at a very high rate even at temperatures as low as -10 °C. The thermodynamic equilibrium calculated by means of DFT, seemed to be very accurate, because the achieved conversions meet the calculated results. As long as the catalyst exhibited a certain activity, the selectivity was always close to 100%. When the activity dropped during the formation of carbonate counter ions, the product selectivity was also decreased. However, the only detectable side-products were the two intermediate products, which could be transformed into the desired products by recycling them. The service time of the tested catalysts was only about one week. By then, most of the active hydroxide counter ions were replaced by less active carbonate counter ions. However, a full regeneration of the catalyst was possible by washing with diluted alkali hydroxide solutions. Therefore it could be concluded, that strong basic ion exchange resins in their hydroxide forms exhibit a superior activity compared to other weakly basic or acidic ion exchange resins.

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